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<b>(21) International Application Number:</b> PCT/GB95/00249 <b>(22) International Filing Date:</b> 7 February 1995 (07.02.95)  <b>(30) Priority Data:</b> PCT/GB94/00228 7 February 1994 (07.02.94) WO (34) Countries for which the regional or international application was filed: AT et al. 9415907.6 5 August 1994 (05.08.94) GB  <b>(71) Applicant (for all designated States except US):</b> WARWICK INTERNATIONAL GROUP LIMITED [GB/GB]; Wortley Moor Road, Leeds LS12 4JE (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> CROUD, Vincent, Brian [GB/GB]; 28 Woodland Drive, Greenfield, Holywell, Clwyd CH8 7HZ (GB). TOMPSETT, Stephen, James [GB/GB]; 5 Lower Bonc Terrace, High Street, Trelawnyd, Nr Rhyl, Clwyd LL18 6DR (GB).  <b>(74) Agent:</b> GILL JENNINGS & EVERY; Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).		<b>(81) Designated States:</b> AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> PROCESS FOR BLEACHING TEXTILES  <b>(57) Abstract</b>  The use of N-acyl and O-acyl bleach activator compounds to generate peroxy acids in aqueous acidic environments usually under relatively dilute conditions. The product is used in situ as a textile bleaching agent. A process for combined desizing and bleaching step optionally includes amylase enzyme in the aqueous acidic environment.		

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## Process for bleaching textiles

5       The present invention relates to a process for bleaching textiles in which an activator is used during a peroxide bleaching step carried out at a pH which is acidic or slightly alkaline. The process is usually part of a multi-step process.

10       In the processing of textile materials either in the form of a yarn or, after further processing in the form of a rope, twine or a fabric which has been prepared by weaving or knitting, it is well known that before such textile materials can be dyed or printed, impurities need to be removed so that they do not interfere with the access  
15       of dyes or other chemicals to the fibres, and to remove any substances which may discolour these fibres. Generally, synthetic fibres are formed in a relatively clean state, having few impurities and requiring little pre-treatment. Natural fibres tend to include a relatively high proportion  
20       of impurities and therefore removal of impurities is especially important in the case of natural fibre textiles.

      The present invention is particularly directed to the treatment of cellulose-based fibres, in particular natural fibres such as cotton, flax and silk, particularly cotton.

25       One stage in textile manufacture may be spinning of fibres to form a yarn. In subsequent processing steps, yarn may be directly bleached and dyed or it may undergo further processing, for example be formed into rope, twine or woven or knitted to form fabric, prior to further  
30       treatment steps such as bleaching and dyeing. When weaving fibres size is often added to the yarn in order to improve handleability. For weaving warp yarns especially require protection and size is added to protect the yarn and to lubricate it to enable more efficient weaving. In finished  
35       fabric, size may therefore be incorporated as an impurity. Fibres may also contain starch, wax, l af or seed husk

fragments which have become entrapped in the cotton yarn and other natural impurities.

The process treatments which may then be required (depending upon the end use) include desizing to break down  
5 any size present; scouring in order to complete removal of any natural or added fats and waxes, also seeds and husks, by oxidation and alkali to obtain fabric in a uniformly absorbent state which is especially necessary for subsequent dyeing and subsequently bleaching.

10 Where the size is starch-based, desizing processes may use starch-digesting (amylase) enzymes in order to break down the starch size. Where the size may be for example polyvinyl alcohol or carboxymethyl cellulose (CMC) -based, in desizing an oxidising agent is contacted with the fibre.

15 Scouring is conventionally carried out by treatment using a hot alkaline solution in the presence of soap or detergent to saponify fat and wax which can then be removed by washing. Both batch and continuous processes are known and the conditions and concentrations of chemicals used are  
20 adapted to the processing technique.

Following scouring, a fabric may require bleaching in order to obtain a high degree of whiteness for goods that are to remain white or are to be dyed to pastel shades and to improve the appearance of the fabric by the  
25 discolouration of any husks or seed coat remaining in the fibre. Bleaching agents which are commonly used include sodium hypochlorite, hydrogen peroxide and sodium chlorite.

Sodium hypochlorite is used in an aqueous alkaline liquid. Bleaching is carried out at ambient temperatures  
30 and must be combined with an effective pre-scouring step. However hypochlorite is unpleasant to handle and impurities left in the fabric, particularly proteins can form unstable compounds with the hypochlorite which can result in gradual yellowing of the finished fabric.

35 Sodium chlorite bleaching is carried out under acidic conditions and whilst it does provide effective bleaching, it is unpleasant and strongly corrosive.

Hydrogen peroxide has more recently become the most widely used bleaching agent as it overcomes the problems of waste disposal and environmental hazards which accompany the hypochlorite and chlorite processes. Hydrogen peroxide textile bleaching processes are generally carried out at  
5 relatively high temperature and in the presence of alkali.

In EP-A-0584710, a process for bleaching textile grey goods ( i.e. yarn formed into fabric) is described in which the textile material is treated in an aqueous liquor  
10 containing a bleach activator such as TAED and hydrogen peroxide. The processes are carried out under alkaline conditions, but the description mentions that the pH range of the bleaching liquor is 5 to 13.

Since hydrogen peroxide degrades to water, it is more  
15 environmentally desirable than other types of textile bleaching materials. In addition to hydrogen peroxide, other peroxygen based bleaches have been used for textile bleaching. However, the use of high alkalinity or high temperatures, especially with long contact times is  
20 undesirable because it tends to cause fibre damage. When fibres which have been treated under highly alkaline conditions are damaged, in subsequent dyeing stages, it is difficult to effect uniform dying.

Furthermore, in the finishing stages of textiles,  
25 often acidic treatment steps are carried out and the use of an acidic bleaching stage is particularly advantageous because no intermediate neutralisation stage is required. Acidic bleaching is therefore desirable because not only does it cut down on the process steps required, but in  
30 addition waste products from the process are reduced.

In American Dyestuff Reporter, June 1992, 34-41 El-Sisi et al describe the activation of hydrogen peroxide used in the preparation of cotton fabrics in a desizing, bleaching and scouring step by urea. The effect of varying  
35 the pH between 4 and 10 is investigated. The concentration of peroxide is always 8g/l(0.24M) or less. The temperature of the reaction is 95°C. In this reaction urea is not a

bleach activator for hydrogen peroxide but instead forms an adduct with hydrogen peroxide to enhance its stability.

For example in US-A-3551087, a specialised process involving simultaneous dyeing and bleaching of wool fibres is described in which performic acid is used as the oxidising agent to effect bleaching. The performic acid is preferably formed in situ from hydrogen peroxide and a formic acid ester or amide.

In DE 4035053 peracetic acid is used under acidic conditions to bleach cotton and other cellulosic materials. The process uses microwaves to enhance bleaching effect and the peracetic acid solution is added directly to the bleaching bath. Peracetic acid however, is explosive and difficult to handle and safer alternatives are required.

Caro's acids are described in WO90/14336 in which carboxylic acids are reacted with hydrogen peroxide dissolved in highly concentrated sulphuric acid. It is suggested in this specification that the acids can be used in textile bleaching. However, there is no disclosure of the specific conditions which should be used.

In FR-A-1176059, acetic acid or acetic anhydride are used with oxygenated water under acidic conditions for textile bleaching. GB 901687 describes a combined scouring and bleaching process for textiles carried out under acidic conditions in which hydrogen peroxide and acetic anhydride are reacted in the presence of an nitrogenous base to produce peracetic acid to effect the scouring and bleaching. An alkaline pre-treatment is suggested. The bleaching temperatures are from 60°C to 90°C.

US-A-3374177 describes the use of performic acid, formed in situ and used under acid to neutral conditions. The use of peracetic acid for fabric bleaching under acidic conditions is also described in GB-A-111736, US-A-3227655 and IN 123143.

In the Textile Research Journal, May 1988, James W Rucker and David M. Cates, pages 148-160, describe catalysis of peracetic acid to bleach cotton fibres at low

temperatures. The peracetic acid is formed in situ from acetic anhydride and hydrogen peroxide with borate present in solution. Kinetic studies are carried out on the effect of pH on the rate of decomposition of the hydrogen peroxide down to a pH of 5.34.

In DE-A-2227602 it is reported that peroxide bleaching under acidic conditions does not produce such effective bleaching on textiles as alkaline peroxide bleaching. This reference overcomes the problem and aims to improve peroxide bleaching using bleach activators chosen from dicarbonates or their derivatives, such as monocarbonates or dialkali metal salts of carbonic acid.

However, a wider range of activators which are suitable for providing effective peroxygen bleaching under acidic conditions, and which will operate over a wider pH range are desirable, to reduce fabric damage and dyeability of textiles. Further, bleaching steps which can be operated at low temperatures are also required.

In accordance with the present invention there is provided a process for textile manufacture comprising obtaining fibres,

(a) forming the fibres into a yarn in a first step;  
(b) in a second step reacting a peroxygen source and a bleach activator compound which is an acyl donor in aqueous solution, to form a product solution comprising an oxidising compound which is a stronger oxidising agent than the peroxygen source, the step being carried out at an acidic pH below  $pK_a(1)$  where  $pK_a(1)$  is the  $pK_a$  of the carboxylic acid corresponding to the acyl group of the activator; and

(c) in a third step, contacting the yarn with the product solution at an acidic pH no greater than  $pK_a(1)$ , in which the bleach activator is a N-acyl compound having at least two carbon atoms in the acyl group.

It has been found that the present invention produces effective bleaching with shorter residence times (i.e.

contact time of the yarn with the bleaching composition), even at very low temperatures.

An additional advantage is that as well as reducing fabric damage during bleaching, the use of acidic conditions also prevents exposing the yarn to pH-shock. Generally, when alkaline bleaching conditions are used, the fibres expand due to the alkali. Since dyeing steps are generally acid, on subsequent contact with the dye the fibres shrink and this leads to problems such as dye-retention which are overcome by this invention.

As used herein, yarn refers to yarn in its state as produced or having undergone additional process steps. Between the first and second, and second and third steps, respectively, other additional, optional textile processing steps may be included. Additional process steps are especially likely to be included between the first and second steps. Examples of the additional steps include weaving, desizing, scouring, washing, rinsing and sequestering steps.

Particularly preferred activators are bleach activators having the compound formula I



in which  $\text{R}^1$  is an alkyl, alkaryl, aralkyl, alkenyl or aryl group, any of which groups have up to 24 carbon atoms and may be substituted or unsubstituted and  $-\text{NR}^2\text{R}^3$  is a leaving group in which  $\text{R}^2$  and  $\text{R}^3$  are independently selected from H,  $\text{C}_{1-24}$ -alkyl, -alkenyl, -aralkyl, -alkaryl or -aryl groups, and carbonyl-containing moieties having at least two carbon atoms in which the carbonyl group is joined to the nitrogen atom in I in which  $\text{R}^2$  and  $\text{R}^3$  can be joined together as a cyclic group and/or  $\text{R}^1$  can be joined to either  $\text{R}^2$  or  $\text{R}^3$  to form a cyclic group. Preferably  $\text{R}^1$  is an aliphatic group, most preferably being a  $\text{C}_{1-18}$ -alkyl or -alkenyl, or is an aryl group. Preferably, the activators have at least two carbon atoms in the acyl group.



In accordance with a further process for textile manufacture as described above, instead of the bleach activators mentioned above, the bleach activator is an ester of a C<sub>2</sub> or higher carboxylic acid and the peroxygen source is present at a concentration of less than 10 M in the aqueous solution. Preferred bleach activators within this category are activator compounds having formula II



in which R<sup>1</sup> is as defined above and R' is selected from C<sub>1-24</sub> alkyl, aralkyl, alkaryl and aryl groups, any of which are substituted or unsubstituted, R<sup>1</sup> and R' optionally being joined to form a cyclic group. Particularly preferred bleach activators within this category are those in which R<sup>1</sup> is selected from methyl and C<sub>4-24</sub> alkyl.

In accordance with a further aspect of the process of the invention, the bleach activator may be any acyl donor and the peroxygen source is present in the aqueous solution in the second step at a concentration of less than 20 M.

Preferably the peroxygen source is reacted with an activator compound in the second step in aqueous solution at a pH below 7, or even below pH 6. The pK<sub>a</sub> of the carboxylic acid corresponding to the acyl group of the activator may be for example up to pH 9 but is generally less than 8.5 or even 8.

The activator may be an N-acyl or an O-acyl derivative. Preferably the activator is a compound of the formula III



in which L is a leaving group attached via an oxygen or a nitrogen atom to the C=O carbon atom and R<sup>1</sup> is an alkyl, aralkyl, alkaryl, or aryl group, any of which groups has up to 24 carbon atoms and may be substituted or unsubstituted.

The leaving group L is preferably a compound the conjugate acid of which has a pKa in the range 4 to 13, preferably 7 to 11, most preferably 8 to 11.

It is preferred that R<sup>1</sup> is an aliphatic group preferably a C<sub>1-18</sub> alkyl group, or an aryl group.

In the present invention the term alkyl includes alkenyl and alkyl groups may be straight, branched or cyclic.

In the formula III L and R<sup>1</sup> may be joined to form a cyclic compound, usually a lactone or a lactam. These cyclic groups may include heteroatoms, for instance oxygen or optionally substituted nitrogen atoms, carboxyl groups as well as -CH<sub>2</sub>- groups or substituted derivatives thereof. They may be saturated or unsaturated. L can itself comprise a cyclic group, including heterocyclic groups, for instance joined to the C=O group of the compound I via the heteroatom.

Substituents on R<sup>1</sup> and L can include hydroxyl, =N-R<sup>2</sup> in which R<sup>2</sup> is selected from any of the groups represented by R<sup>1</sup> and is preferably lower alkyl, amine, acyl, acyloxy, alkoxy, aryl, aroyl, aryloxy, aroyloxy, halogen, amido, and imido groups and the like as well as other groups not adversely affecting the activity of the compound.

In the invention the compound of the formula I can be any N-acyl or O-acyl acyl-donor compound, which has been described as a bleach activator for use in laundry detergents. The compound of the formula I may be an anhydride, but is preferably an ester or, even more preferably, an amide derivative.

Amide derivatives include acyl imidazolides and N,N-diacylamides, such as TAED. Other examples of N-acyl derivatives are:

a) 1,5-diacetyl-2, 4-dioxohexahydro-1,3,5-triazine (DADHT);

b) N-alkyl-N-sulphonyl carbonamides, for example the compounds N-methyl-N-mesyl acetamide, N-methyl-N-mesyl

benzamide, N-methyl-N-mesyl-p-nitrobenzamide, and N-methyl-N-mesyl-p-methoxybenzamide;

c) N-acylated cyclic hydrazides, acylated triazoles or urazoles, for example monoacetyl maleic acid hydrazide;

5 d) O,N,N-trisubstituted hydroxylamines, such as O-benzoyl-N,N-succinyl hydroxylamine, O-p-nitrobenzoyl-N,N-succinyl hydroxylamine and O,N,N-triacetyl hydroxylamine;

e) N,N'-diacyl sulphurylamides, for example N,N'-dimethyl-N,N'-dimethyl-N,N'-diacetyl sulphuryl amide and  
10 N,N'-diethyl-N,N'-dipropionyl sulphurylamide;

f) 1,3-diacetyl-4,5-diacyloxy-imidazolines, for example 1,3-diformyl-4,5-diacetoxy imidazoline, 1,3-diacetyl-4,5-diacetoxy imidazoline, 1,3-diacetyl-4,5-dipropionyloxy imidazoline;

15 g) Acylated glycolurils, such as tetraacetyl glycoluril and tetrapropionyl glycoluril;

h) Diacylated 2,5-diketopiperazines, such as 1,4-diacetyl-2,5-diketopiperazine, 1,4-dipropionyl-2,5-diketopiperazine and 1,4-dipropionyl-3,6-dimethyl-2,5-  
20 diketopiperazine;

i) Acylation products of propylene diurea and 2,2-dimethyl propylene diurea, especially the tetraacetyl or tetrapropionyl propylene diurea and their dimethyl derivatives;

25 j) Alpha-acyloxy-(N,N')polyacyl malonamides, such as alpha-acetoxy-(N,N')-diacetyl malonamide.

k) O,N,N-trisubstituted alkanolamines, such as O,N,N-triacetyl ethanolamine.

k') Cyanamides, such as those disclosed in DE-A-3,304,848.

30 l) N-acyl lactams, such as N-benzoyl-caprolactam, N-acetyl caprolactam, the analogous compounds formed from C<sub>4-10</sub> lactams.

m) N-acyl and N-alkyl derivatives of substituted or unsubstituted succinimide, phthalimide and of imides of  
35 other dibasic carboxylic acids, having 5 or more carbon atoms in the imide ring.

Alternatively the compound may be an ester, for instance

- n) sugar esters, such as pentaacetylglucose,
- o) esters of imidic acids such as ethyl benzimidate,
- 5 p) triacylcyanurates, such as triacetylcyanurate and tribenzoylcyanurate,
- q) esters giving relatively surface active oxidising products for instance of  $C_{8-18}$ -alkanoic or -aralkanoic acids such as described in GB-A-864798, GB-A-1147871 and the
- 10 esters described in EP-A-98129 and EP-A-106634, for instance compounds of the formula I where L comprises an aryl group having a sulphonic acid group (optionally salified) substituted in the ring to confer water solubility on a benzyl group, especially nonanoyloxy-
- 15 benzenesulphonate sodium salt (NOBS), isononanoyloxy-benzenesulphonate sodium salt (ISONOBS) and benzoyloxy-benzenesulphonate sodium salt (BOBS)
- r) phenyl esters of  $C_{14-22}$ -alkanoic or -alkenoic acids,
- s) esters of hydroxylamine,
- 20 t) geminal diesters of lower alkanoic acids and gem-diols, such as those described in EP-A-0125781 especially 1,1,5-triacetoxypent-4-ene and 1,1,5,5-tetraacetoxypentane and the corresponding butene and butane compounds, ethylidene benzoate acetate and bis(ethylidene acetate)
- 25 adipate and
- u) enol esters, for instance as described in EP-A-0140648 and EP-A-0092932.

Where the activator is an anhydride it is preferably a solid material, and is preferably an intra-molecular anhydride, or a polyacid polyanhydride. Such anhydride

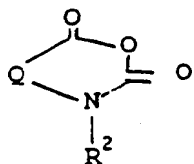
30 compounds are more storage stable than liquid anhydrides, such as acetic anhydride. Anhydride derivatives which may be used as activator include

- v) intramolecular anhydrides of dibasic carboxylic
- 35 acids, for instance succinic, maleic, adipic, phthalic or 5-norbornene-2,3-dicarboxylic anhydride,

11

w) intermolecular anhydrides, including mixed anhydrides, of mono- poly-basic carboxylic acids, such as diacetic anhydride of isophthalic or perphthalic acid

x) isatoic anhydride or related compounds such as  
5 described in WO-A-8907640 having the generic formula II

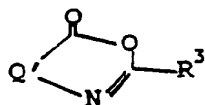


II

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wherein Q is a divalent organic group such that Q and N together with the carbonyl groups and oxygen atom of the anhydride group form one or more cyclic structures and R<sup>2</sup>  
15 is H, alkyl, aryl, halogen or a carbonyl group of a carboxyl containing function; or benzoxazin-4-ones as described in WO-A-8907639, that is compounds of the formula III

20



III

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wherein Q' is selected from the same groups as Q and R<sup>3</sup> is H, alkyl, aryl, alkaryl, aralkyl, alkoxy, haloalkyl, amino, aminoalkyl, carboxylic group or a carbonyl-containing function; preferably 2-methyl-(4H)3,1-benzoxazin-4-one (2MB4) or 2-phenyl-(4H)3,1-benzoxazin-4-one (2PB4);

30

y) polymeric anhydrides such as poly(adipic) anhydride or other compounds described in our co-pending application WO-A-9306203.

35

The peroxygen source may be hydrogen peroxide itself, or an inorganic persalt, for instance a percarbonate or, a perborate, for instance sodium perborate, or an organic peroxide such as benzoyl peroxide or urea peroxide. Mixtures of any of these peroxygen sources may also be used. A particularly preferred peroxygen source is hydrogen peroxide.

In the perhydrolysis reaction of the second step the amount of water present is preferably at least as much (in terms of moles) as the peroxygen source. Where the peroxygen source is hydrogen peroxide itself, the concentration of hydrogen peroxide is preferably less than 70% weight/volume (that is weight of hydrogen peroxide based on volume of water plus hydrogen peroxide plus other components in the mixture). Preferably the concentration is less than 60% weight by volume and more preferably less than 30% w/v. Where the product of the reaction is to be used in a domestic environment or other environment where it is difficult to take special precautions in handling the products, it is preferred for the concentration to be less than 15% or even 10% w/v or less than 5% w/v. The concentration is usually at least 0.2%, preferably at least 1% w/v, more preferably at least 2% w/v. Where the peroxygen source is other than hydrogen peroxide then the concentration is preferably such as to give the equivalent available oxygen as the quoted concentrations of hydrogen peroxide. The concentration of peroxygen source in the aqueous liquid is for instance less than 20M or even less than 10M, preferably less than 5M or sometimes even less than 3M down to 0.01M. Preferably the concentration is at least 0.05M, more preferably 0.1M, even more preferably at least 0.2M.

The pH in the third, bleaching step is usually less than 7.0, preferably less than 6.0 or even less than pH 5. The pH is usually more than 2.0, preferably more than 3.0.

In the process of the invention it is possible for the second step to be carried out with a time delay before the third step commences. For instance the peroxygen source and the bleach activator may be allowed to react in aqueous conditions for at least five minutes, up to one or two days, suitably in the range ten minutes to one day before the aqueous reaction product of the second step is contacted with textiles to be used as a bleaching composition. The peroxygen source and bleach activator may

be mixed together and added to water simultaneously, or alternatively they may be added to water one after the other or in various combinations. They may be added to water and used immediately.

5       The fibres which are formed into a yarn in the first step of the process (preferably by spinning) of the present invention may be any natural or synthetic fibre. However, preferably the invention relates to cellulose-based fibres such as cotton, flax, hemp, jute, rayon and acetate. The  
10       invention is particularly directed to processes in which the fibres are natural cellulose-based fibres such as cotton.

      In the third step of the process according to the present invention the yarn may be contacted with the  
15       product solution in the form of a yarn or, alternatively, having undergone further processing for example, in the form of rope, twine, non-woven or preferably woven or knitted fabrics.

      In the third step of the present invention, contact of  
20       the yarn with the product solution may be by any means. Contact will be using any of the batch, semi-continuous or fully continuous methods known in the industry. For example for batch-wise processing, the product solution may be held in a kier which is usually fully enclosed and  
25       pressurised. The batch-wise processes using a kier, generally the bleaching liquor will be sprayed on to the top of the textile and allowed to percolate to the bottom of the kier where it is pumped out and recirculated. Alternative batch processes may be carried out using a jig  
30       or a winch.

      Semi-continuous processes which may be used include, for example pad-steam-roll and pad-roll techniques or any other semi-continuous process known for carrying out conventional bleaching steps for textile bleaching. In  
35       a pad-steam-roll method, the yarn is impregnated with the bleaching solution on a saturator and the excess removed by squeezing on a mangle. The wet yarn is then passed through

a steaming chamber where it is warmed to raise the temperature to for example above 80°C generally around 100°C. The yarn is then rolled into a rotating bath which is generally fully enclosed in a chamber and filled with steam to maintain the temperature. Generally the batch is rotated at the high temperature for 3 to 4 hours. In a pad-roll technique, the yarn is impregnated with the bleaching solution and excess is removed by squeezing on a mangle. The wet yarn is then rolled into a large batch where it is stored for up to 24 hours at room temperature.

Generally, in continuous processes known in textile manufacturing, the yarn is impregnated with the bleaching solution and the steam to raise its temperature. It is then stored for a period of time sufficient to allow bleaching, generally up to 1 hour, preferably from 2 to 30 minutes.

The present invention is particularly directed to use in a pad-batch process or in a pad-steam process.

The time taken in any of the processes described above depends upon the yarns for bleaching; the amount and nature of the impurities and the temperature of the process. However, contact of the yarn with the product solution will be for sufficient time to permit effective bleaching.

The invention is particularly useful because it enables effective bleaching even at low temperatures and therefore in the bleaching step, preferably the temperature will not be significantly greater than 60°C, most preferably no greater than 40°C. Thus, a particular advantage of using the activators for the peroxygen source is that the oxidising product tends to be formed at a relatively low temperature, for instance at temperatures around ambient and less than hand hot (37°C) or even below 25 or 20°C or even as low as 5°C, which is advantageous from both a safety and an energy-saving point of view. The present invention also includes a process in which the bleaching step may also provide scouring or desizing.



Therefore, desized or unsized yarn will be contacted with the product solution in the third step and the duration of contact and the temperature of contact will be sufficient to permit effective scouring and bleaching.

5 Notwithstanding the above, the invention may be used at higher temperatures, up to 95°C, whilst retaining the other benefits of the invention.

The processes of the present invention provide effective bleaching and optionally also scouring and in addition can be used at low temperatures. The compositions used are advantageous in that fibre damage is reduced compared with known processes, particularly compared with alkaline bleaching processes. In a preferred process, subsequent to the third bleaching step, the yarn is dyed.

10 Any textile dye and any conventional dyeing process may be used.

The present invention also provides use of an oxidising composition comprising a peroxygen source and an activator which is an acyl donor preferably having at least two carbon atoms in the acyl group and, if necessary an acidifying component such that when the composition is added to water the peroxygen source, the activator and the acidifying component dissolve and the pH is reduced to and remains below pH 7, the use of such composition being to

20 bleach yarn in textile manufacture. Preferably, the use is prior to dyeing textiles.

The oxidising composition may contain a pH-adjusting component which may comprise a polybasic organic acid, such as a polybasic carboxylic acid such as succinic or adipic acid, in addition to citric and/or sulphamic acid.

30 Alternatively the component may react with a by-product of the perhydrolysis reaction to increase the acidity in use. Where perborate is used, borate is a by-product and so any component known to react with borate to drop the pH, e.g. cis-1,2-diols, such as glycols, boric acid or sodium

35 dihydrogen phosphate can be used. Such acidifying

components are also suitable for use where percarbonate is the peroxygen source.

5 In one preferred embodiment of the oxidising composition the activator is TAED. The peroxygen source is preferably hydrogen peroxide.

10 Although the oxidising composition for use in the present invention may contain the individual components each in separate compositions, for instance one of which contains the peroxygen source, another of which contains the activator and another of which contains the pH-modifying component, it is preferred to provide at least the activator and pH-modifying component as a mixture in a single composition in a form in which they are stable. Such a composition which does not contain peroxygen source, 15 may, for instance, be added to an aqueous solution of peroxygen source such as aqueous hydrogen peroxide, which is readily commercially available, in the form of, for instance 60%, 20%, 10% or, preferably, 5% w/v or less solution. It is most preferred for all of the components 20 to be provided in a single composition, in which the components do not react, and which is preferably therefore substantially water-free.

The compositions may be in liquid form, for instance in a non-aqueous liquid medium, in which the components may 25 be dissolved or dispersed. For instance particles of activator with protective coatings, for instance produced by microencapsulation techniques or spray coating of solid activator, may be suspended in an aqueous, or non aqueous, solution of peroxygen source. As an alternative to a 30 solution of peroxygen source that component may also be suspended in the liquid medium, either in a separate liquid phase or in particulate dispersed phase, particles of solid peroxygen source optionally being coated with a protective coating. Coated particles of either peroxygen source or 35 activator may be disrupted or diluted into water or with abrasion.

Preferably the oxidising composition is in a solid form, for instance as a mixture of particles of the individual components or, more preferably, comprising particles each of which comprise all of the components.

5 Such particles may be provided by techniques similar to those used in the laundry detergent industry, for instance including particles produced by spray drying liquid slurries, by granulation techniques using binders (for instance synthetic or natural polymers or derivatives) or

10 by melt blending followed by extrusion or other techniques.

Preferably the product contains the active ingredients in appropriate relative quantities so that when the composition is diluted (or the compositions are mixed) with water the first step of the reaction proceeds at the

15 optimal rate and at the desired pH. The activator and peroxygen source are for instance present in relative amounts such that up to 500%, preferably 5% to 150% of the stoichiometric amount of activator (for complete reaction with the peroxygen source) is provided. Preferably the

20 amount of activator is 10 to 100%, more preferably 20 to 80% of the stoichiometric amount.

The product solution may require surface active properties. Where they are required, the product solution may comprise a surfactant. Any conventional surfactant may

25 be used, selected from non-ionic, anionic, cationic, and amphoteric surfactants. However, non-ionic and amphoteric surfactants are preferred as they are more resistant to changing conditions of pH and water hardness. Particularly preferred surfactants are those which have good rinsing

30 properties and which can therefore be rinsed easily from the textile after treatment.

Suitable nonionic surfactants include for example alkanolamides (such as C10 to C20) and/or ethoxylated alcohols, carboxylic acids, amines, alcohol amides, alcohol

35 phenol, glyceryl esters, sorbitan esters, phosphate esters etc.

Suitable amphoteric surfactants include for example betaines, such as alkyl betaines, sulphobetaines, and also imidazoline derivatives.

5        Suitable cationic surfactants include for example quaternary amines, imidazolines and quaternised imidazolines.

10        Suitable anionic surfactants include any surfactant useful in a detergent for example salts of sulphonic or monoesterified sulphuric acids, fatty alkyl ether sulphosuccinates, acyl sarcosinates, acyl taurides and paraffin sulphonates. The preferred anionic surfactants are salts of alkali metals or alkaline earth metals, preferably sodium.

15        Where the oxidising composition comprises surfactant it is preferably in amount no greater than 5% by weight surfactant, most preferably no greater than 3% by weight surfactant, based on the total weight of the oxidising composition.

20        The compositions of the present invention may also include a chelating agent. One or mixtures of more than one chelating agent can be used. Particularly preferred chelating agents are EDTA, DTPA and phosphonates.

25        The oxidising composition may include other additives, for instance stabilisers which stabilise the product before use, as well as stabilisers for the peroxy acid oxidising species formed in the reaction, such as any heavy metal sequestrant. In addition to the surfactants mentioned above, inorganic salts, for instance which affect the physical properties of the solid form or act as diluent may also be incorporated. Other ingredients may be included depending upon for example the mode of use of the composition. Examples are agents to assist dissolution or dispersion of the product into water, or metal or catalysts.

35        The oxidising compositions of the present invention may be provided in a form which is suitable to be diluted

directly into water to allow the second and third steps of the reaction to proceed without further additions.

The oxidising compositions of the present invention may be either solid or liquid. For example, they may be pourable liquids which are aqueous or non-aqueous, or may be in any other form. Preferably, the compositions are either solid or a pourable liquid. Thickeners may be included to increase viscosity, such as those which are well known in the art, including gums, electrolytes (in combination with surfactant), urea, triethanolamine and polyacrylates.

The oxidising compositions for use in the present invention are preferably low foaming and therefore, if surfactant is included de-foaming agents may be incorporated, such as soap or silicone anti-foams.

The solid oxidising compositions according to the invention are particularly preferred because they have good storage stability since in general it is easier to keep the bleach activator and peroxygen donor compound in separate particles, and is easier to isolate other components of the composition from one another and from the bleach components.

In the solid compositions, one or more of the components may be in a granular form and these granules may include agents to increase the rate of dissolution of the compositions upon addition to water. Such dissolution rate enhancers may create effervescence, for instance, a suitable component may be sodium bicarbonate or other alkaline metal bicarbonates.

In accordance with a further aspect of the present invention there is provided a process for textile manufacture comprising obtaining fibres and forming them into a yarn and subjecting the yarn to a desizing step and a bleaching step, comprising reacting a peroxygen source with an activator compound which is an acyl donor in aqueous solution at a pH below  $pK_a(1)$  to form a product solution comprising an oxidising compound which is a

stronger oxidising agent than the peroxygen source, contacting the yarn with the product solution at an acidic pH below  $pK_a(1)$  to effect bleaching in the bleaching step; and in the desizing step, contacting the yarn with an aqueous acidic desizing composition.

In accordance with a further aspect of the present invention there is provided a process for textile manufacture comprising obtaining fibres and forming them into a yarn and subjecting the yarn to a combined desizing and bleaching step, in which the desizing and bleaching step is as the bleaching step described above and the product solution described above effects both desizing and bleaching, optionally also effecting scouring.

In accordance with a further aspect of the present invention there is provided a process for textile manufacture comprising obtaining fibres and forming them into a yarn and subjecting the yarn to a desizing step, in which the desizing step is as the bleaching step described above and the product solution described above effects desizing, optionally also effecting scouring.

Generally the desizing composition will be an oxidative composition. The desizing composition may however comprise amylase enzymes for digesting starch containing sizes. Therefore, when the desizing composition is an oxidising composition, preferably the product solution is used as the desizing and bleaching composition so that desizing and bleaching (optionally also with scouring) are effected in one step. Thus, the contact time and temperature for contacting the yarn with the product solution will be sufficient to effect desizing and bleaching, optionally also scouring.

The claimed process may be carried out having a rinsing step between the desizing and the bleaching steps. The desizing step may be carried out using either cold, warm or steam working conditions. Cold conditions are generally carried out at a temperature of from 20 to 40°C, although the temperature may be up to 50°C, over a period

of from 4 to 16 hours at a pH of around 4.5 to 7.0; warm desizing conditions are generally at temperatures from around at 60 to 70°C for a period of from 3 to 6 hours and across a pH of from 5.0 to 7.0; and steam working  
5 conditions generally rely upon temperatures from 100 to 105°C, for a period of 1 to 5 minutes and over a pH of 5.0 to 7.5. A steam step may be prior to during or after contact of the yarn with the product solution.

Where the desizing step is carried out separately it  
10 will generally comprise steps of impregnation of the yarn with the desizing composition to degrade the size (either by enzymic hydrolysis for the starch-based sizes or by oxidation of non-starch based sizes) and a rinsing step to rinse off the degradation product. The desizing step may  
15 be a batch step for example using a jig or winch, it may be a semi-continuous process such as a pad-roll or pad-batch process or may be a continuous process using a J-box or steam chamber.

In a further aspect of the invention, the size will be  
20 a starch-based size and the desizing and bleaching steps are combined. The combined step may also provide scouring.

In this preferred aspect of the invention, a process for textile manufacture is provided comprising

(a) obtaining fibres and forming them into a yarn,  
25 (b) in a second step, reacting a peroxygen source and a bleach activator compound which is an acyl donor in aqueous solution to form a product solution comprising an oxidising compound which is a stronger oxidising agent than the peroxygen source, the second step being carried out at  
30 a pH below  $pK_a(1)$  where  $pK_a(1)$  is the  $pK_a$  of the percarboxylic acid corresponding to the acyl group of the activator and

(c) in a third step, contacting the yarn with the product solution at pH no greater than  $pK_a(1)$  and in the  
35 presence of a starch-digesting enzyme.

Preferably the pH in both steps (b) and (c) will be below 7, preferably below 6.5, or even below 6.

For enzymatic desizing, an enzyme is generally impregnated into the yarn by immersion in an aqueous solution containing enzyme. Generally, the enzyme will be present in the solution at a concentration of from 1 to 20 g/l, preferably around 2 to 10 g/l in a pad-batch process, it is conventional use pad-batch processes in which the textile is rolled up and stored for a period, as described above. The temperature and time for storage may vary but should be sufficient to enable the enzyme to break down the starch-based size. The storage temperature is preferably at ambient conditions at room temperature. The immersion temperature is often higher than the storage temperature and may be up to for example 70°C or even 100°C but should not be so high that the enzyme is inactivated. After the combined desizing/bleaching step, preferably, prior to further processing such as dyeing, the fabric or yarn is washed to remove the degraded products. In the alternative pad-steam process, after impregnation of the yarn or fabric with enzyme, the impregnated textile is contacted with steam at a temperature generally from 102°C to 110°C, most usually from 102°C to 105°C, for 2 to 6 minutes or for sufficient time to enable the enzyme to effect degradation of the starch-based size and the textile is subsequently washed to remove degraded size.

The contact time for the yarn with the product solution in the third step will be for sufficient time to effect desizing, scouring and bleaching or, where no scouring is needed, to effect desizing and bleaching. The contact time will vary depending upon the temperature of contact with the aqueous liquid will preferably be in a cold pad-batch process in which the yarn (which has optionally been further processed before treatment to be made into a fabric for example by weaving or knitting) is contacted with the desizing/bleaching product solution from the second step at an initial temperature above 50°C, for up to 2 minutes and subsequently, excess bleaching/sizing product solution is removed and the yarn is rolled up and



maintained in a moist condition for up to 48 hours, generally no greater than 24 hours and most preferably for up to 10 hours at ambient temperatures.

Where the contacting process involves a steaming step, the temperature of the initial contact of the product solution with the yarn achieves temperatures of up to 110°C. If that temperature is maintained, contact may only be required for up to 30 minutes, generally for no greater than 15 minutes and most preferably for no greater than 10, or even 7 minutes.

In accordance with a further aspect of the invention, yarn which has not undergone a desizing step and which includes either a starch, polyvinyl alcohol or carboxymethyl cellulose-type size may undergo desizing, scouring and bleaching simultaneously using the product solution formed in the second step. Thus, in a preferred aspect of the present invention, the fibre which has been formed into yarn is sized with a starch, polyvinyl alcohol, carboxymethyl cellulose or any other type of size which can be degraded by oxidation, and no desizing step has been undergone prior to contact of the yarn with the product solution, in the third step.

The following examples illustrate the invention. In the example, the concentration of the peroxygen source is reported in terms of the starting concentration of aqueous hydrogen peroxide, to which other reactants are added. The molar concentration of the mixtures can be calculated.

#### Example 1

##### Reaction of TAED and hydrogen peroxide

1.1 This area of investigation was to find a simple method of determining the presence of a stronger oxidising species than hydrogen peroxide. To this end a number of indicators containing oxidisable groups were tried, to identify which changed colour on addition of peracetic acid and the oxidising product of an embodiment of the invention, but not hydrogen peroxide. The results showed that alizarin complexone (AC) was decolorised by peracetic acid, but not

by hydrogen peroxide. This material was therefore selected as the indicator of choice.

1.2 Once an indicator had been identified it was possible to carry out the experiments to see whether acid catalysed perhydrolysis was a possible mechanism. TAED (22.8g 0.1mol) was added to 60% hydrogen peroxide (60mls 1mol). The mixture was stirred for 10 minutes. A 2ml aliquot was removed and added to alizarin complexone solution (0.5ml). Over a period of a few minutes the colour in the solution was seen to disappear as the indicator was bleached.

1.3 The successful result of this experiment led to comparative bleaching experiments being carried out on stained swatches of cotton cloth. The stains used were Red Wine, Tea and BC1 (tea and clay). Comparisons were made between the bleaching performance of 60%  $H_2O_2$ , 10% peracetic acid PAAH and TAED/ $H_2O_2$ . The performance was assessed by measuring the initial brightness before washing and final brightness using a Hunterlab D25M colorimeter after the swatches had been rinsed and dried by application of an electric iron set at the wool setting. The results are given in Table 1.

1.4 Another set of experiments determined at which initial pH was the greatest bleaching observed. These experiments were carried out in 60ml 60%  $H_2O_2$  with 22.8g TAED added. The pH of the peroxide was adjusted before the addition of TAED with sodium hydroxide. The highest pH attainable was 6.95 as above this the decomposition of the peroxide was too rapid. The stain used in these tests were tea stains produced in house. These were selected as they showed the greatest residual colour in the previous tests. The pH of the solutions were measured initially after 1 hour's bleaching after 3h and finally after 24h. All bleaching experiments were carried out at room temperature. A blank was run using distilled water at pH 6. The results are shown in Tables 2 and 3.

1.5 Experiments were also carried out to identify whether Fe(III) ions had an effect on the bleaching properties.

Three systems were set up, one containing Dequest 2066 (an alkylene polyamine poly(methylene phosphonic acid) as a sequestering agent, one with 0.5mls 20mM Fe(III) solution added and one with hydrogen peroxide only. All of these were carried out at pH 6. The results are shown in Table 3.

#### 1.6 Results & Discussion

All experiments carried out at room temperature in open beakers. Dwell time in the bath of 1 hour.

Table 1

Example	Stain	Red Wine		Tea	
		Initial Brightness	Final Brightness	Initial Brightness	Final Brightness
1.1	TAED/H <sub>2</sub> O <sub>2</sub> 60%	46.5	74.8	25.0	63.9
1.1 comp	H <sub>2</sub> O <sub>2</sub> Comp	46.5	69.7	25.8	46.6
1.2 comp	PAAH	46.5	76.7	25.7	61.0
1.3 comp	HCl	46.5	63.9	-	-

Table 2

BCl Stains (Tea and Clay)

Example		pH after time				Initial Brightness	Final Brightness
		Initial	0.5hr	1.5hr	46hr		
1.2	Bleaching solution						
	TAED/60% H <sub>2</sub> O <sub>2</sub>	1.21	1.28	1.71	2.64	38.5	53.8
1.4 Comp	60% H <sub>2</sub> O <sub>2</sub>	1.21	-	-	-	38.5	48.9

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Table 3

Tea Stains	Example	Bleaching solution	pH after time				Initial Brightness	Final Brightness
			Initial	1hr	3hr	24hr		
5	1.3	TAED/60% H <sub>2</sub> O <sub>2</sub>	2.5	2.48	3.12	2.68	25.8	72.8
	1.4	TAED/60% H <sub>2</sub> O <sub>2</sub>	3.15	2.76	3.40	2.71	24.9	76.1
	1.5	TAED/60% H <sub>2</sub> O <sub>2</sub>	4.54	3.03	3.30	2.68	26.8	77.8
	1.6	TAED/60% H <sub>2</sub> O <sub>2</sub>	5.13	3.18	3.20	2.70	24.9	79.1
	1.7	TAED/60% H <sub>2</sub> O <sub>2</sub>	6.0	3.33	3.26	2.80	24.4	82.9
10	1.8	TAED/60% H <sub>2</sub> O <sub>2</sub>	6.95	3.58	3.70	3.35	24.8	84.8
	1.9	TAED/60% H <sub>2</sub> O <sub>2</sub> /Seq	6.05	2.83	2.65	-	26.8	82.7
	1.5 Comp	60% H <sub>2</sub> O <sub>2</sub> /Fe(III)	6.22	6.07	6.08	-	24.3	75.6
	1.6 Comp	60% H <sub>2</sub> O <sub>2</sub>	6.19	6.11	6.13	-	25.4	75.8
	1.7 Comp	Deionised Water	5.96	-	-	-	23.4	33.7
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- Notes: With 60% hydrogen peroxide and TAED at the higher end of the acidic pH range bleaching was visible on contact, with the other solutions the bleaching was much less rapid. On reaction there was effervescence visible as the TAED dissolved, this process was much more rapid at higher pH. There was a distinct odour of peracetic acid from all reactions containing TAED. Remarkably the bleaching activity towards AC was still observed after 24 hours at room temperature.
- 1.7 These results show that TAED activates peroxide solutions at a range of pH's. The quickest bleaching performance is seen at higher pH probably due to more rapid dissolution of TAED and formation of stronger oxidising species under these conditions. The formation of an acidic species when TAED is dissolved in hydrogen peroxide is indicated by the pH change observed, the solutions only become markedly more acidic if TAED is present. Those experiments carried out without TAED show very little change in pH on the same time scale. The noticeable odour of peracetic acid, which is rather distinctive as well as pungent, is also evidence for the presence of this species in solution. It is assumed from this evidence that peracetic acid is likely to be the bleaching/oxidising species responsible for the bleaching effect, although it may be a by-product, an intermediate or the product of further reaction of another oxidising species.
- 1.8 The experiments with and without Fe(III), at pH 6, showed very similar bleaching (the %ge stain loss was identical). This seems to show that iron catalysed radical reactions are not important under these conditions. This conclusion is borne out by the results with sequestrant present which gave very similar results to the experiment without sequestrant at pH 6.

Example 2

TAED, DADHT and SNOBS as activators for peroxygen bleaches at acidic pH, for stains in solution and on fabrics

2.1 Experimental

## 5     2.1.1         Swatches

The activator/peroxygen source combination procedure used was 60% hydrogen peroxide in a 10:1 ratio with the activator. Small swatches of cotton cloth (20-25cm<sup>2</sup>) were used and the stain was chlorophyll. The bleaching  
10 experiments were run using 10mls hydrogen peroxide (60%) which was adjusted to the required pH using sodium hydroxide solution. A weighed quantity of the activator (16.7 mmol) was then added and the mixture stirred for 2 minutes to dissolve the activator. The swatch of cloth was  
15 then added and left for 30 minutes with occasional stirring. After 30 minutes, the swatches were removed from the activator solutions, rinsed with deionised water to remove any remaining traces of bleach, dried by the technique used in example 1 and the brightness measured  
20 using a Hunterlab D25M colorimeter. The pH of the solution was measured after the cloths had been removed. The results are shown in Table 4.

## 2.1.2         The dependence of pH on time

Experiments to monitor the relationship between pH and  
25 time were carried out using TAED, DADHT and SNOBS as activators. The pH of 60% hydrogen peroxide was adjusted to about pH 6. To 20mls of this solution was added 33m mols of activator. The pH was measured with time.

## 2.1.3         Timed bleaching

30         Timed bleaching experiments were carried out using the same technique and quantities as in 2.1.1 above with different dwell times of the swatch in the bleach solution. Six separate solutions were prepared and a swatch added to each at the same time. The swatches were removed and  
35 rinsed in deionised water after set time periods. The times used were 5mins, 10mins, 20mins, 30mins, 1hr and 2hrs. The final brightness after drying by the usual

technique was determined using the Hunterlab. The results are shown in Table 5.

#### 2.1.4 Time/pH bleaching profile

5 The solutions and swatches used were prepared as in the above experiments. Four solutions were prepared and a swatch added to each after a set period of time. The cloth was left in the bleach solution for 5mins and then removed and rinsed thoroughly with deionised water. The times at which the swatches were added were after 1min, 15mins, 10 30mins and 1hr. A different solution was used for each swatch. The activators used were TAED and DADHT. The final brightness after drying of the cloth was measured using the Hunterlab. The results are shown in Table 7.

#### 15 2.1.5 Activation of sodium perborate solutions in the presence of acidifying components.

Two lots of sodium perborate tetrahydrate (17.5g) mixed with citric acid (8g) (to reduce the pH on reaction with borate) were prepared. To one lot TAED (2.6g) was added. Each of the mixtures was added to 50mls deionised 20 water and stirred vigorously. The pH of the solutions was measured after dissolution had been achieved. The results are given in 2.2.6 below.

Sodium perborate tetrahydrate (20g) was mixed with sodium dihydrogen phosphate (17.5g) (to reduce pH). SNOBS 25 (4.4g) was added. The mixture was added to 100ml deionised water and a chlorophyll stained swatch added to each solution. After 1.5hrs the swatch was removed and the brightness measured on the Hunterlab. The pH was measured at timed intervals.

### 30 2.2 Results and Discussion

2.2.1 The chlorophyll stain was seen to be resilient to bleaching under these harsh conditions which makes it a very good stain to use. The less stain that is removed the better the comparisons which can be drawn between bleaches.

35 2.2.2 SNOBS gave the quickest results with DADHT fairly close behind. TAED reacted slowest, see table 7. It should be noted however, that the activat rs are used on



equivalent molar basis (i.e. equivalents of acyl group released) so that the weight of TAED is less than, for instance, the weight of SNOBS. The blank experiments with peracetic acid, water and hydrogen peroxide (at both pH 6 and pH 1) show that activation is occurring, when the activator is present, and that this is not an effect of the lower pH in the activated solutions (Table 4). The drop in pH is good evidence that an acidic species is being produced which is not present in the unactivated peroxide solution.

2.2.3 The decrease in pH on addition of activator was seen to be rapid (Table 6). As would be expected the rate varied with different activators due to differences in both the acid being produced and the rate of perhydrolysis.

2.2.4 The bleaching of swatches with different bleaching times showed the expected increase of bleaching with time (Table 5).

2.2.5 The effect of time and pH on the bleaching efficacy of activated solutions was also studied. In this case the dwell time in the bleaching solution was the same (5 mins) but the swatches were added after different times. In four separate solutions cloth was added after 1min, 15mins, 30mins and 1hr. Each of these swatches was a quarter of the same larger swatch, to ensure a constant substrate concentration. After 5 minutes in the bleaching solution the cloth was removed and rinsed with deionised water. Comparing of the different swatches, for the same activator, gave a measure of the stability, rate of peracid release and pH dependence of the bleaching. The relationship between these variable is complex but qualitative comparisons can be made. The results show that TAED gives consistent bleaching over the first hour. DADHT on the other hand gives better initial bleaching but after an hour the efficacy was similar (Table 7). This seems to show that DADHT is perhydrolysed more rapidly initially but after time gives a similar concentration of peracid. This is borne out by the pH measurements. The pH of the

solution containing DADHT decreased more rapidly than that of the TAED containing solution. After 20hrs the figures were much closer (Table 6).

5 2.2.6 SNOBS was seen to give better bleaching at all times in this test, i.e. up to 2 hours. The release of strong oxidising species seemed to be slow. The cloth added after 1min showed less bleaching than those added later (Table 2). In all cases the stability of the bleach activation with time was remarkably good. There was  
10 noticeably better bleaching than with peroxide alone in all cases.

2.2.7 The activation of sodium perborate solutions was also seen to occur under acidic conditions. The use of citric acid and sodium dihydrogen phosphate enable acidic  
15 solutions of perborate to be prepared which also give rise to some degree of buffering. When SNOBS was incorporated into such a solution there was noticeably quicker bleaching than occurred without any added activator. The pH of the solutions was seen to be acidic (pH 5.1) and much more  
20 stable than seen with more concentrated peroxide solutions. The pH of the activated and unactivated solutions was very similar.

Table 4. Activating acidic peroxide with different activators.

Example	Activator	Initial pH	Final pH	Initial Brightness	Final Brightness
2.1	TAED (30min)	6.00	2.47	14.26	38.4
2.2	SNOBS	6.00	2.58	14.26	72.4
2.3	DADHT	6.00	2.33	14.26	61.3
2.1 Comp	Blank (H <sub>2</sub> O <sub>2</sub> )	6.00	5.96	14.26	30.9
2.2 Comp	Blank (H <sub>2</sub> O)	7.50	5.68	14.26	19.7
2.3 Comp	Blank (PAAH)	-	-	14.26	59.2
2.7	TAED (10min)	6.00	-	14.26	21.8

Table 5. The effect of different bleaching times on brightness and solution pH.

Time/ mins	Final brightness			pH after 2 hrs		
	TAED	DADHT	SNOBS	TAED	DADHT	SNOBS
5	27.8	48.8	47.8	3.21	3.15	3.64
10	33.5	57.4	58.7	3.09	3.15	3.64
20	46.2	60.6	80.8	3.20	3.17	3.53
30	52.2	68.2	81.5	3.15	3.15	3.51
60	57.1	79.8	82.6	3.18	3.21	3.61
120	74.1	84.5	81.9	3.21	3.14	3.50

Table 6. The effect of activators on solution pH with time.

Time/ mins	pH		
	TAED	DADHT	SNOBS
0	6.18	6.05	6.05
1	5.29	4.83	5.16
2	5.03	4.50	5.01
3	4.85	4.23	-
5	4.62	3.96	4.81
7	4.47	-	-
9	4.35	-	-
10	4.31	-	-
20	4.00	-	-
23	-	3.26	-
24	-	-	4.44
30	3.86	-	-
40	-	3.11	4.18
65	3.64	-	-
107	-	-	3.95
1200	3.27	2.54	-

Table 7. Bleaching efficiency against time.

Time/ mins	Initial Brightness	Final Brightness		
		TAED	DADHT	SNOBS
1	14.26	32.0	34.1	42.6
15	14.26	31.9	32.7	40.6
30	14.26	28.7	26.9	54.3
60	14.26	25.8	20.9	53.3

DADHT - 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine

SNOBS - sodium nonanoyloxybenzene sulphonate

### Example 3

#### Acids and anhydrides as activators

##### 3.1 Using acetic acid (comparative) and TAED (invention) as the acetyl donor.

The following experiments were carried out using 50ml 10% w/v hydrogen peroxide at room temperature with

activator and compared against controls. Chlorophyll stained cotton swatches were used as the substrate. Reflectance was measured using an ICS Texicon Spectra Flash 500 (a colorimeter using the CIELAB system) using software version 4.70.

The initial pH's of these solutions were recorded.

The swatches were left in solution for 75 minutes. The brightness was compared to an unbleached chlorophyll stained swatch after rinsing with deionised water and drying as in the previous examples.

### Results

Table 8

Example	Reading	Solution	Activator	Initial, pH
3.1.1	1.6 lighter	50 ml H <sub>2</sub> O <sub>2</sub>	TAED 3.17g	3.35
3.1.2 Comp	0.35 lighter	50 ml H <sub>2</sub> O <sub>2</sub>	Glacial Acetic 1.67g	2.32
3.1.3 Comp	0.75 lighter	50 ml H <sub>2</sub> O <sub>2</sub>	-	3.33
3.1.4 Comp	0.2 darker	50 ml H <sub>2</sub> O	Glacial Acetic 1.67g	2.62

It can be seen that acetic acid is ineffective as an activator under these conditions. This experiment also shows that the bleaching effect of TAED does not arise from hydrolysis followed by perhydrolysis of the resulting acetic acid.

### 3.2 The use of acetic anhydride (comparative) and TAED (inventive)

Acetic anhydride is a widely used source of peracids under laboratory conditions. This material is however water sensitive, corrosive and therefore not easy to handle. The following experiments were designed to see how effective acetic anhydride was as a peracid generator under dilute aqueous conditions.

The procedure used was similar to that in the above experiments (5.1) with acetic acid. Hydrogen peroxide was

used at 10%. A range of stained swatches were used, these were chlorophyll, curry and blackberry. Samples were also assayed for peracetic acid using an iodometric titration.

### 3.2.1 Bleaching stained swatches

5 In the following experiments the peroxide/activator combinations shown in Table 10 were used to prepare the bleaching solutions.

10 All experiments were carried out at ambient temperature. Formulation 3.2.4 Comparative was only used in the first two experiments. The reflectance was measured as in 3.1. In the table the reflectance differences are noted. A positive value means the bleached swatch is lighter than the control stained swatch and a negative sign means it is darker.

#### 15 Experiment A

Chlorophyll stained swatches were added to these solutions and left to bleach for 75 mins. After this time the swatches were removed and washed in water to remove any remaining active species.

#### 20 Experiment B

Chlorophyll stained swatches were added to the solutions used above and left to bleach overnight for 17 hours. The swatches were rinsed. The pH of the bleaching solution was measured after the cloths had been removed.

#### 25 Experiment C

Fresh solutions using the first three compositions were prepared and allowed to stand overnight before chlorophyll stained swatches were added. The cloths were left to bleach for 75 mins and then removed and rinsed.

#### 30 Experiment D

This was the same as experiment A but using curry stained swatches. There was no water/acetic anhydride solution (3.2.4 comp) tested.

#### Experiment E

35 This was the same as experiment A using blackberry stained swatches. There was no water/acetic anhydride solution (3.2.4 comp) tested.

## 3.2.2 Results

Table 9

Experiment	Solution	Activator	pH	Reflective Difference				
				A	B	C	D	E
3.2.1	50ml H <sub>2</sub> O <sub>2</sub>	3.17g TAED	3.47	1.3	4.4	0.38	1.3	8.6
3.2.2 Comp	50ml H <sub>2</sub> O <sub>2</sub>	2.4g acetic anhydride	2.10	3.2	8.6	1.6	1.3	10.2
3.2.3 Comp	50ml H <sub>2</sub> O <sub>2</sub>	-	3.69	0.6	1.0	0.67	1.2	8.2
3.2.4 Comp	50ml H <sub>2</sub> O	2.4g acetic anhydride	-	0.48	-0.4	-	-	-

In general acetic anhydride/H<sub>2</sub>O<sub>2</sub> reacted more quickly than either TAED/H<sub>2</sub>O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> itself. TAED/H<sub>2</sub>O<sub>2</sub> gave better bleaching against chlorophyll stains than H<sub>2</sub>O<sub>2</sub> alone.

Example 4

Beaker experiments were undertaken to determine the optimum bleaching conditions of pH, temperature and bleaching time required to bleach desized, scoured cotton using TAED/peroxide. The performance of a bleaching solution containing TAED/peroxide was compared with a solution containing peroxide alone under identical conditions. Experiments carried out at 20°C and 40°C were monitored over a 24 hour period. Experiments undertaken at 60°C were monitored over a five hour period. The effect of pH was evaluated between 5 and 6.9 and temperature was assessed at 20°C, 40°C and 60°C, respectively. The TAED used in the bleaching experiments was in the form of MYKON ATC (supplied by the applicant company) and labelled ATC in the figures.

Method

For each test 1000g deionised water was weighed into a two litre heavy duty pyrex beaker. Into the same beaker, 10g of sodium hydrogen also phosphate were added, followed by 2g of Lutensit Alba, then 1g Dequest 2066 sequestering

agent was added. The solution was stirred and 30ml hydrogen peroxide (60% w/v) 200 volumes was added and the solution adjusted to the desired pH using pre-sequestered sodium hydroxide. The sodium hydroxide was pre-sequestered by weighing 995g of sodium hydroxide (46/48%) into a two litre glass beaker, followed by 5g Dequest 2066. After stirring vigorously for five minutes using a magnetic stirrer the sodium hydroxide solution was stored on an empty plastic container and left to stand for a minimum of 24 hours before use.

After the pH adjustment using pre-sequestered sodium hydroxide, 1.0g of MYKON ATC were added and the beaker was placed on a hot plate for the 40°C and 60°C experiments only) and stirred vigorously. When the desired temperature was obtained, stirring was continued for fifteen minutes, whilst maintaining a constant temperature.

Three cotton swatches were then placed in the solution and stirred gently for the required bleaching time, whilst maintaining a constant temperature. After completion of the bleaching time, the swatches were removed and rinsed in two litres of hot tap water (65-75°C) for one minute, then a further two litres of cold tap water for one minute. The swatches were then air dried and after 24 hours CIE whiteness readings were taken using a Spectraflash spectrophotometer.

### Results

The results are represented graphically in Figures 1 to 3 which illustrate CIE whiteness, versus Bleaching Time (hours).

From the results, it can be seen that the incorporation of a bleach activator into a bleaching solution gives rise to superior bleaching than can be obtained by peroxide alone at all the temperatures over the whole bleaching period.

At pH 5, the incorporation of bleach activator gives rise to superior bleaching than that obtained by peroxide alone at all temperatures and bleaching times. At 20°C,



the maximum whiteness achieved by peroxide alone after 24 hours, is achieved by the combination of bleach activator/peroxide after only five hours.

5 Incorporation of the activator into a bleaching solution at 40°C, enables a similar level of whiteness to be achieved after only two hours of bleaching time compared with the bleaching time of 24 hours peroxide alone.

10 At pH 6, at 60°C, the CIE whiteness achieved by peroxide alone is 48.7 after five hours of bleaching. This whiteness can be achieved by the activator/peroxide bleaching composition at 20°C after 24 hours, or at 60°C with a reduced bleaching time of two hours.

15 At pH 6.9, superior bleaching for the activator/peroxide bleaching compositions were obtained at 20°C, 40°C and 60°C. It can be observed that the activator/peroxide at 20°C shows superior bleaching to peroxide alone at 40°C.

20 The results illustrate that the present invention can substitute the use of higher temperatures therefore increasing safety and reducing energy costs.

CLAIMS

1. A process for textile manufacture comprising obtaining fibres,

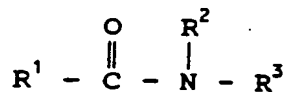
5 (a) forming the fibres into a yarn in a first step;

(b) in a second step reacting a peroxygen source and a bleach activator compound which is an acyl donor in aqueous solution to form a product solution comprising an oxidising compound which is a stronger oxidising agent than the peroxygen source, the step being carried out at an acidic pH below  $pK_a(1)$  where  $pK_a(1)$  is the  $pK_a$  of the percarboxylic acid corresponding to the acyl group of the activator; and

10 (c) in a third step, contacting the yarn with the product solution at an acidic pH no greater than  $pK_a(1)$ , in which the bleach activator is an acyl donor having at least two carbon atoms in the acyl group.

2. A process according to claim 1 in which the bleach activator is an N-acyl compound, preferably of the formula

20 I



I

25 in which  $R^1$  is an alkyl, aralkyl, alkaryl or aryl group, any of which groups have up to 24 carbon atoms and may be substituted or unsubstituted, and  $-NR^2R^3$  is a leaving group in which  $R^2$  and  $R^3$  are independently selected from H,  $C_{1-24}$ -alkyl, -aralkyl, -alkaryl or -aryl groups, and carbonyl-containing moieties having at least two carbon atoms in which the carbonyl group is joined to the nitrogen atom in I, in which  $R^2$  and  $R^3$  can be joined together as a cyclic group and/or  $R^1$  can be joined to either  $R^2$  or  $R^3$  to form a

30 cyclic group, preferably,  $R^1$  being an aliphatic group, most preferably a  $C_{1-18}$  alkyl group, or is an aryl group.

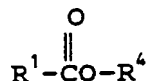
3. A process according to claim 1

in which the bleach activator is an ester of a  $C_2$  or higher carboxylic acid and the peroxygen source is present

at a concentration of less than 10M in the aqueous solution.

4. A process according to claim 1 in which the peroxygen source is reacted with an activator compound having formula

5 II



II

10 in which R<sup>1</sup> is as defined above and R<sup>4</sup> is selected from C<sub>1-24</sub>-alkyl, aralkyl, alkaryl and aryl groups, any of which are substituted or unsubstituted, R<sup>1</sup> and R<sup>4</sup> optionally being joined to form a cyclic group, preferably R<sup>1</sup> being selected from methyl and C<sub>4-24</sub>-alkyl.

15 5. A process according to any preceding claim in which the activator compound is a solid at room temperature.

6. A process according to any preceding claim in which the third step takes place at a temperature below 60°C, preferably below 50°C.

20 7. A process according to any preceding claim in which the second step is carried out at a pH less than 7, preferably in the range 2.0 to 6.5, more preferably in the range 5.0 to 6.5.

8. A process according to any preceding claim in which  
25 the peroxygen source is present in the reaction mixture for the second step at a concentration of less than 10M, preferably less than 5M, more preferably less than 1M.

9. A process according to any preceding claim in which  
30 the activator is present in the aqueous solution which is the perhydrolysis reaction mixture in an amount less than the stoichiometric amount for reaction with the peroxygen source.

10. A process according to any preceding claim in which  
35 the second step is carried out in the presence of an acid-generating species.

11. A process according to any preceding claim in which prior to the third step, the fabric undergoes a desizing step in acidic conditions in the presence of an enzyme.

12. A process for textile manufacture comprising obtaining fibres and forming them into a yarn and subjecting the yarn to a combined desizing and bleaching step,

5        reacting a peroxygen source with an activator compound which is an acyl donor in aqueous solution at a pH below  $pK_a(1)$  to form a product solution comprising an oxidising compound which is a stronger oxidising agent than the peroxygen source, and contacting the fabric with the  
10       product solution at a pH below  $pK_a(1)$ .

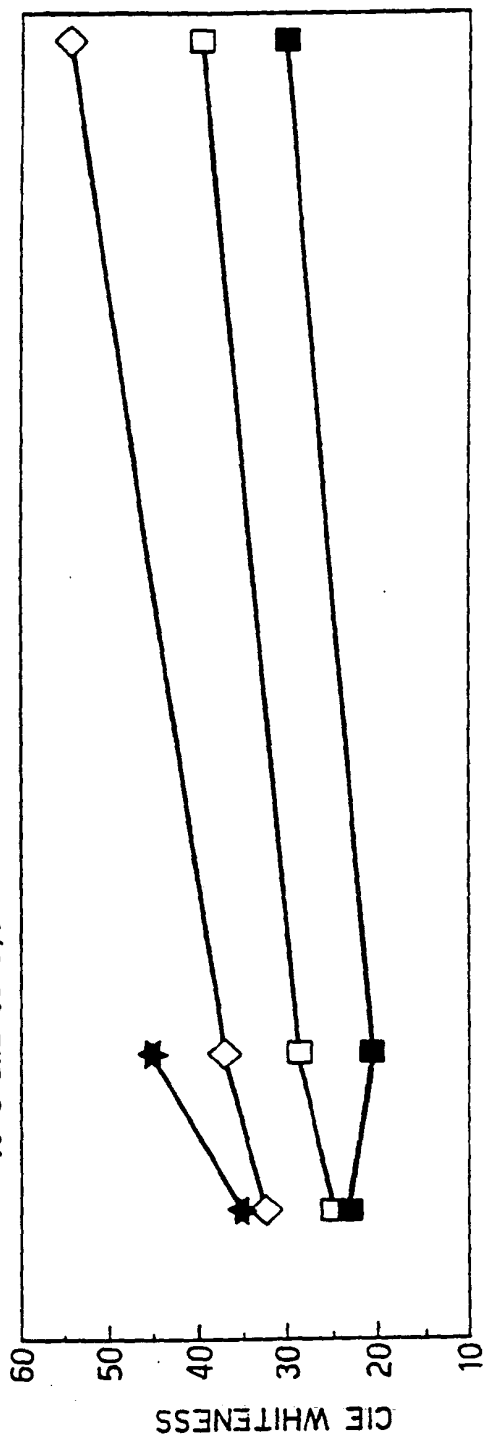
13. A process for textile manufacture comprising reacting a peroxygen source with an activator compound which is an acyl donor in aqueous solution at a pH below  $pK_a(1)$  to form a product solution comprising an oxidising compound which  
15       is a stronger oxidising agent than the peroxygen source, and contacting yarn comprising starch containing size, with the product solution which comprises amylase enzyme, at a pH below  $pK_a(1)$ , to effect bleaching and desizing, and preferably also scouring.

20       14. A process according to claim 13 in which the amylase enzyme is present during the reaction between the peroxygen source and the bleach activator, preferably the amylase enzyme being present in the product solution at a concentration from 1 to 10g/l.

25

Fig.1.

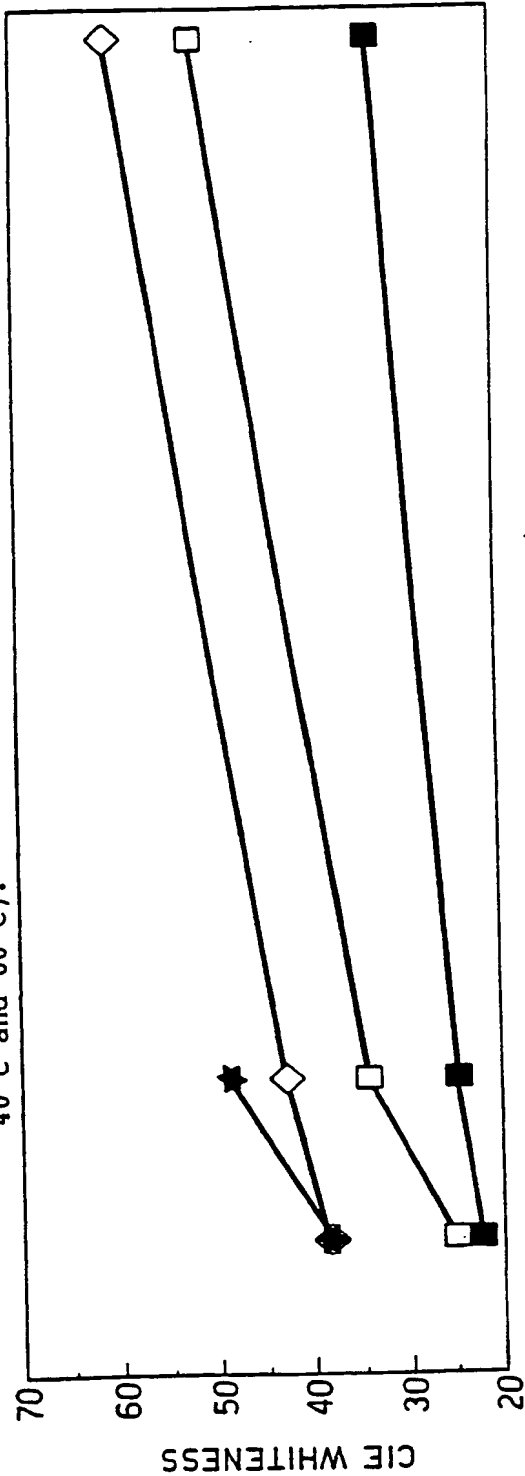
Peroxide Alone and Peroxide with ATC at pH 5 (20°C,  
40°C and 60°C).



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Fig.2.

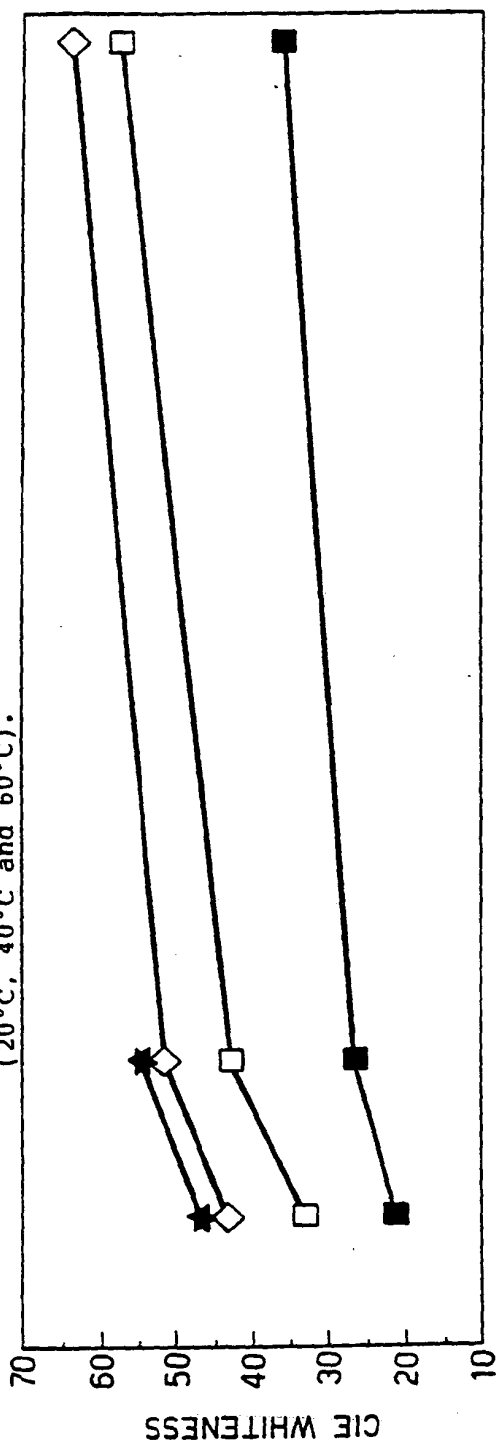
Peroxide Alone and Peroxide with ATC at pH 6 (20°C, 40°C and 60°C).



Bleaching Time (HRS)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
H2O2 20°C			22.90			24.82																			32.88
H2O2 40°C			32.58			36.16																			47.82
H2O2 60°C			38.21			48.72																			51.25
H2O2/ATC 20°C			25.41			34.12																			60.24
H2O2/ATC 40°C			38.63			42.80																			
H2O2/ATC 60°C			41.81			51.75																			

Fig. 3.

Peroxide Alone and Peroxide with ATC at pH 6.9  
(20°C, 40°C and 60°C).



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# INTERNATIONAL SEARCH REPORT

Internat. Application No.  
PCT/GB 95/00249

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 D06L3/02 C11D3/39 C07C409/26 C07C409/24 C07C409/30

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D06L C11D C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO-A-94 18299 (WARWICK INTERNATIONAL GROUP LIMITED) 18 August 1994 see page 5, line 5 - page 12, line 17; example 1 ---	1,3-10
X	US-A-3 227 655 (K. PRETT ET AL) 4 January 1966 cited in the application see the whole document ---	1,4,6,7
X	GB-A-901 687 (TEXTIL-GESELLSCHAFT MBH ) 25 July 1962 cited in the application see page 1, line 43 - page 4, line 26 --- -/--	1,4,7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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- \*&\* document member of the same patent family

Date of the actual completion of the international search

15 June 1995

Date of mailing of the international search report

21.06.95

Name and mailing address of the ISA

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Authorized officer

Doolan, G



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/LB 95/00249

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO-A-93 12067 (THE PROCTER & GAMBLE COMPANY ) 24 June 1993 see page 4, paragraph 1 - page 10, paragraph 2 ---	1,3,4,6, 7
A	US-A-3 551 087 (O. SCHMIDT ) 29 December 1970 cited in the application see column 1, line 1 - column 5, line 47; examples 9,13 -----	1,2,4,7, 10

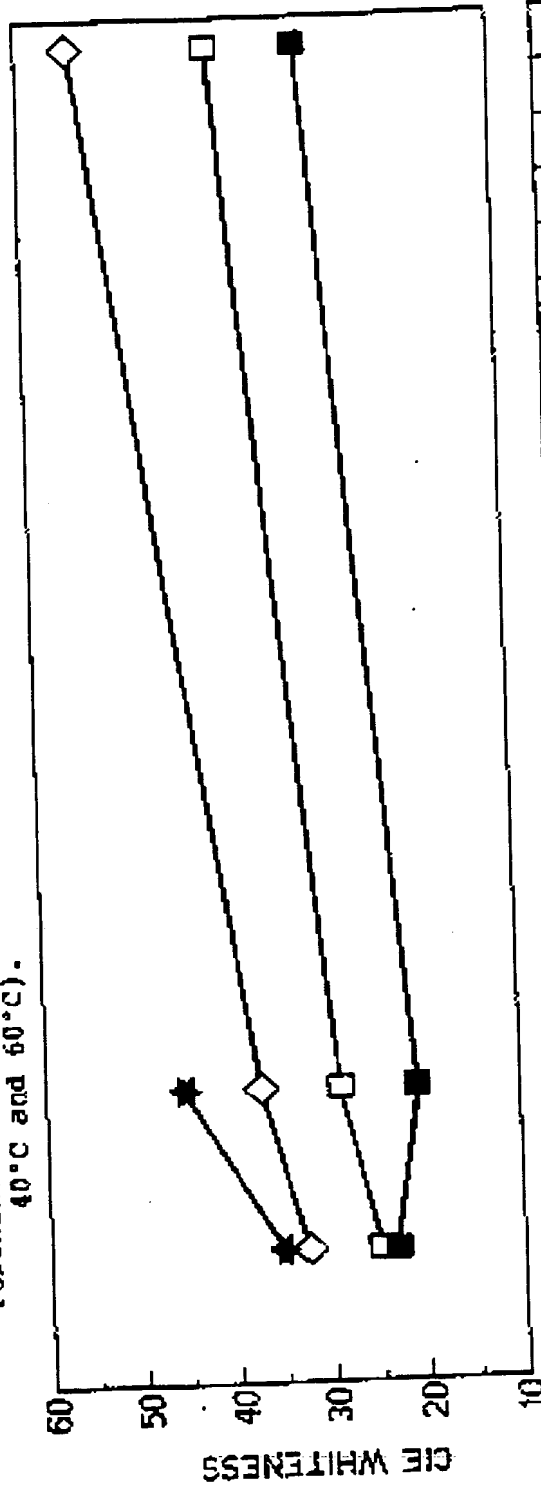
## INTERNATIONAL SEARCH REPORT

 Internat: Application No  
 PCT/Gb 95/00249

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9418299	18-08-94	AU-B- 5976594	29-08-94
US-A-3227655	04-01-66	DE-B- 1158956 FR-A- 1238246 GB-A- 901687	30-11-60
GB-A-901687		DE-B- 1158956 FR-A- 1238246 US-A- 3227655	30-11-60 04-01-66
WO-A-9312067	24-06-93	AU-B- 3237593 CA-A- 2124787 CN-A- 1074477 EP-A- 0624154 JP-T- 7501821 NO-A- 942211	19-07-93 24-06-93 21-07-93 17-11-94 23-02-95 13-06-94
US-A-3551087	29-12-70	BE-A- 666517 CH-B- 450343 CH-B- 479750 CH-A- 880165 DE-B- 1269991 DE-B- 1269993 DE-A- 1469608 DE-A- 1469609 FR-A- 1462230 GB-A- 1064534 NL-A- 6508903 NL-A- 6916024 US-A- 3374177	07-01-66 15-10-69 19-12-68 27-03-69 22-02-67 11-01-66 26-01-70 19-03-68

Fig. 1.

Peroxide Alone and Peroxide with ATC at pH 5 (20°C, 40°C and 60°C).

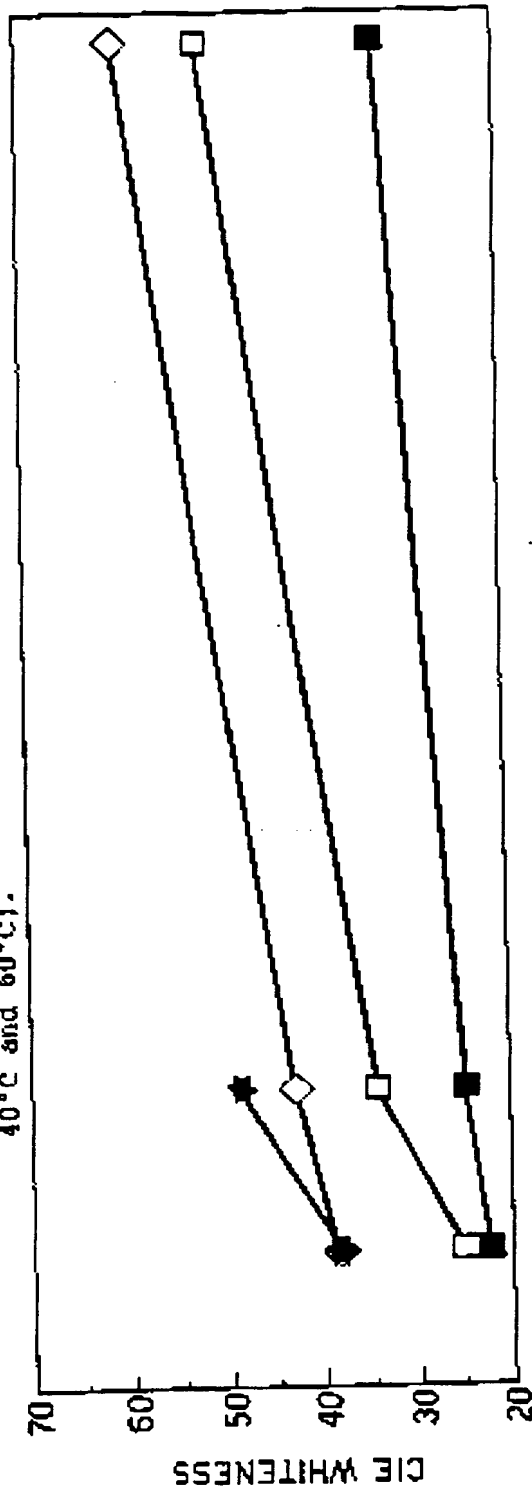


Bleaching Time (Hrs)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
H <sub>2</sub> O <sub>2</sub> 20°C		23.27				29.76																			29.76
H <sub>2</sub> O <sub>2</sub> 40°C		27.10				30.23																			30.23
H <sub>2</sub> O <sub>2</sub> 60°C		26.13				44.92																			44.92
H <sub>2</sub> O <sub>2</sub> /ATC 20°C		24.78				38.62																			38.62
H <sub>2</sub> O <sub>2</sub> /ATC 40°C		32.41				36.07																			36.07
H <sub>2</sub> O <sub>2</sub> /ATC 60°C		35.43				49.34																			49.34

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Fig.2.

Peroxide Alone and Peroxide with ATC at pH 6 (20°C,  
40°C and 60°C).

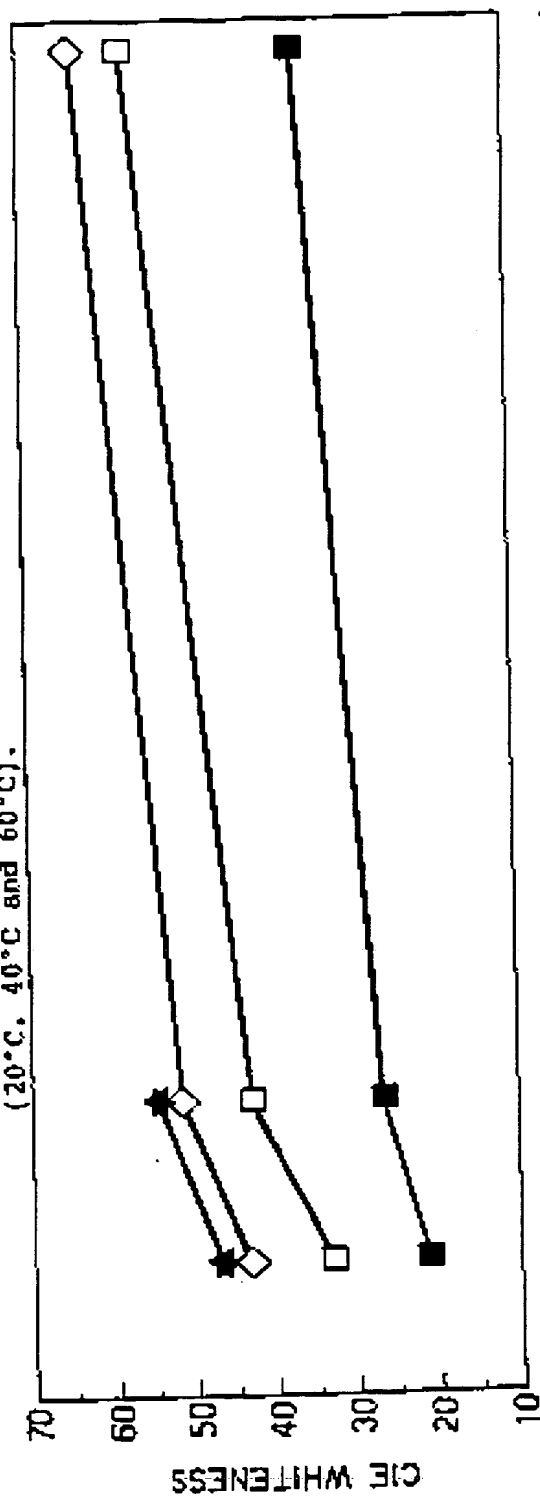


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BLEACHING TIME (HRS)	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
H <sub>2</sub> O <sub>2</sub> 20°C			32.88			34.83																			32.88
H <sub>2</sub> O <sub>2</sub> 40°C			32.88			36.16																			47.82
H <sub>2</sub> O <sub>2</sub> 60°C			32.88			43.72																			51.25
H <sub>2</sub> O <sub>2</sub> /ATC 20°C			25.41			39.12																			40.24
H <sub>2</sub> O <sub>2</sub> /ATC 40°C			36.83			42.80																			
H <sub>2</sub> O <sub>2</sub> /ATC 60°C			41.81			51.75																			

Fig. 3.

peroxide Alone and Peroxide with ATC at pH 6.9  
(20°C, 40°C and 60°C).

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